PROCESS TO PREPARE SYNTHESIS GAS

Field of the invention

The invention is directed to a process to prepare a mixture comprising carbon monoxide and hydrogen from a carbonaceous feed by performing a partial oxidation reaction and an endothermic steam reforming reaction.

Background of the invention

EP-A-168892 describes an endothermic steam reforming reaction, which is carried out in a fixed bed situated in at least one pipe in which a temperature of between 800 and 950 °C is maintained by routing at least part of the hot product gas from a partial oxidation reaction along the pipe(s). According to this publication the combined partial oxidation (POX) and endothermic production of synthesis gas result in a better yield of synthesis gas, an increased H_2/CO ratio, a lower usage of oxygen per m^3 of synthesis gas product obtained and a lower capital cost of the plant for the production of CO and H_2-containing gas mixtures (as compared to partial oxidation).

A reactor and process for performing a steam reforming reaction is described in DE-A-3345088. This publication describes a reactor vessel for performing a steam reforming reaction starting from a natural gas feedstock. The vessel consisted of a tube sheet from which a plurality of tubes filled with a suitable catalyst extended into the vessel. The required heat of reaction is provided by passing the hot effluent of a partial oxidation reaction of natural gas at the exterior of the reactor tubes in the vessel. Such steam reformer

reactors are also referred to as so-called convective steam reformer reactors (CSR).

Suitably there is a desire to operate a convective steam reformer and make use of the hot gasses of a partial oxidation. A problem when combining these processes is that the temperature of the gasses as obtained in a partial oxidation reaction are high, e.g. between 1100 and 1500 °C. If such gasses are to be used to provide the heat in a convective steam reformer practical problems have to be overcome, such as one have to avoid that the materials used in the CSR reactor do not break as a result of mechanical failure. There is thus a desire to obtain a combined POX and CSR process, which overcomes these practical problems.

<u>Summary of the invention</u>

This object is achieved with the following process. Process for the preparation of hydrogen and carbon monoxide containing gas from a carbonaceous feedstock by performing the following steps:

(a) partial oxidation of a carbonaceous feedstock in an vertically oriented tubular partial oxidation reactor vessel comprising a burner at its upper end thereby obtaining a first gaseous product of hydrogen and carbon monoxide,

(b) catalytic steam reforming a carbonaceous feedstock in a Convective Steam Reformer Zone thereby obtaining a steam reformer product,

(c) reducing the temperature of the first gaseous product of step (a) by mixing this product with the steam reformer product of step (b),

(d) contacting the mixture obtained in step (c) with a post reforming catalyst, and

(e) providing the required heat for the convective steam reforming reaction zone in step (b) by convective heat exchange between the mixture obtained in step (d) and the steam reformer reactor zone thereby obtaining a hydrogen and carbon monoxide containing gas having a reduced temperature.

Applicants found that by reducing the effluent of the partial oxidation by mixing with the effluent of the steam reformer and subsequently performing a post reforming step one can run the CSR at a lower temperature. The higher methane content of the steam reformer product as a result of operating the CSR at lower temperatures is balanced by performing the catalytic post reforming step in which part of the methane is converted to synthesis gas.

Description of the Figures

Figure 1 illustrates a POX and a CSR reactor in a configuration according the invention.

Detailed description of the invention

The carbonaceous feedstock in step (a) is preferably a gaseous hydrocarbon, suitably methane, natural gas, associated gas or a mixture of C_{1-4} hydrocarbons. Examples of gaseous hydrocarbons are natural gas, refinery gas, associated gas or (coal bed) methane and the like. The gaseous hydrocarbons suitably comprises mainly, i.e. more than 90 v/v%, especially more than 94%, C_{1-4} hydrocarbons, especially comprises at least 60 v/v percent methane, preferably at least 75 percent, more preferably 90 percent. Preferably natural gas or associated gas is used. Preferably any sulphur in the feedstock is removed.

Preferably the carbonaceous feed in both steps (a) and (b) is a gaseous feed as described above. In such a

preferred embodiment from 10 to 90 wt%, more preferably from 20 to 50 wt%, of the total gaseous feed to steps (a) and (b) is fed to step (b).

In step (a) the partial oxidation may be performed according to well known principles as for example described for the Shell Gasification Process in the Oil and Gas Journal, September 6, 1971, pp 85-90. Publications describing examples of partial oxidation processes are EP-A-291111, WO-A-9722547, WO-A-9639354 and WO-A-9603345. In such processes the feed is contacted with an oxygen containing gas under partial oxidation conditions preferably in the absence of a catalyst.

The oxygen containing gas may be air (containing about 21 percent of oxygen) and preferably oxygen enriched air, suitably containing up to 100 percent of oxygen, preferably containing at least 60 volume percent oxygen, more preferably at least 80 volume percent, more preferably at least 98 volume percent of oxygen. Oxygen enriched air may be produced via cryogenic techniques, but is preferably produced by a membrane based process, e.g. the process as described in WO 93/06041.

Contacting the feed with the oxygen containing gas in step (a) is preferably performed in a burner placed in a reactor vessel. To adjust the H_2/CO ratio in the gaseous product obtained in the partial oxidation reaction in step (a), carbon dioxide and/or steam may be introduced into the feed. Preferably up to 15% volume based on the amount of gaseous product, preferably up to 8% volume, more preferably up to 4% volume, of either carbon dioxide or steam is added to the feed. As a suitable steam source, water produced in an optional downstream hydrocarbon synthesis, e.g. Fischer-Tropsch synthesis, may be used.

The gaseous product of the partial oxidation reaction in step (a) typically has a temperature of between 1100 and 1500 °C and an H_2/CO molar ratio of from 1.5 up to 2.6, preferably from 1.6 up to 2.2.

Step (b) may be performed by well-known steam reforming processes, wherein steam and the gaseous hydrocarbon feed are contacted with a suitable reforming catalyst in a CSR reactor. Preferably the CSR reactor zone is present in a separate reactor vessel next to the POX reactor vessel. The convective steam reactor zone preferably comprises of a tubular reactor vessel provided with one or more tubes containing a reforming catalyst. Various designs for such a reactor are known and suited for the present invention. The design should be such that the steam reformer product and the synthesis gas used to provide heat are obtained as separate streams in such a reactor. An Example of such a reactor concept is described in US-A-6224789. The steam reformer product may have a methane content of between 1 and 30 mol% carbon relative to the carbon as hydrocarbon in the feed to step (b). In a preferred embodiment the methane content is between 1 and 10 mol% carbon and preferably between 2 and 5 mol% carbon relative to the carbon as hydrocarbon in the feed to step (b),

The catalyst and process conditions as applied in the steam reformer reactor tubes may be those known by the skilled person in the field of steam reforming. Suitable catalysts comprise nickel optionally applied on a carrier, for example alumina. The space velocity of the gaseous feed is preferably from 700 to 1000 litre (S.T.P.)/litre catalyst/hour, wherein S.T.P. means Standard Temperature of 15 °C and pressure of 1 bar abs. The steam to carbon (as hydrocarbon and CO) molar ratio

is preferably below 1 and more preferably from 0.5 up to 0.9. If such low steam to carbon ratio's are applied in step (b) the catalyst preferably comprises a Group VIII metal. More preferably the catalyst comprises (a) an oxidic support material and (b) a coating comprising between about 0.1 and about 7.0 wt% of at least one of the metals of the group consisting of Pt, Ni, Pd and Co, preferably platinum; said support material comprising: (i) at least 80 wt% of ZrO_2 which has been calcined at a temperature up to about 670 °C before the application of said coating; (ii) 0.5-10 mol% of at least one oxide selected from the group consisting of Y, La, Al, Ca, Ce and Si, preferably La_2O_3. Examples of such catalysts are for example the catalyst described in EP-A-695279. Preferably the feed also comprises an amount of CO2, wherein preferably the CO2 over carbon (as hydrocarbon and CO) molar ratio is from 0.5 up to 2. The product gas of step (b) preferably has a temperature of from 600 up to 1000 °C and a H2/CO molar ratio of from 0.5 up to 2.5.

In Step (c) the temperature of the first gaseous product of step (a) is reduced by mixing this product with the steam reformer product of step (b). This mixing may be performed in the partial oxidation reactor vessel, in a separate mixing vessel or within a separate CSR reactor vessel. If the mixing is performed in the POX reactor vessel it is preferably performed by feeding the steam reformer product to the lower end, preferably in the lower half of the POX reactor vessel, spaced away from the burner. In this manner no significant methane conversion takes place during mixing and a reduction of temperature will result. Due to mixing at a position spaced away from the burner of the product of the

partial oxidation reaction having a temperature of between 1100 and 1500 °C and steam reformer product having a considerable lower temperature a temperature reduction relative to the temperature of the product of the partial oxidation reaction of between 250 and 500 °C.

In step (d) the mixture obtained in step (c) is contacted with a post reforming catalyst. This may suitably be achieved by passing the gaseous mixture through a bed of suitable reforming catalyst. This catalyst bed may be position in the POX reactor vessel, in a separate vessel or in the CSR reactor vessel, also depending on the location at which step (c) is performed. When step (c) is performed in the POX reactor vessel step (d) is preferably performed in a catalyst bed positioned just below the inlet of the steam reforming product in said vessel.

The methane is preferably converted in a step (d) in which also a temperature reduction is achieved of suitably between 20 and 70 °C and preferably between 40 and 60 °C. The mixture obtained in step (d) having a reduced methane content preferably has a temperature of between 950 and 1100 °C and more preferably a temperature between 980 and 1050 °C. The methane conversion in step (d) is suitably between 10 and 50 wt%.

The catalyst bed may be any well-known reformer catalyst, for example a Ni-containing catalyst or the catalysts as described for step (b).

The effluent of step (d) is subsequently fed to the CSR reactor zone wherein the gasses supply heat to said zone and a cooled final synthesis gas product is obtained. In step (e) the temperature of the metal wall

surfaces of the materials of the internals in the CSR reactor are preferably maintained below 1100 °C.

The above process may be performed in a process configuration as illustrated in Figure 1. Figure 1 illustrates a CSR reactor (44) and a POX reactor vessel (51). The CSR reactor (44) is provided with one or more parallel positioned reactor tubes (21) filled with a bed (22) of steam reforming catalyst, comprising a passageway (23) for hot gas, namely the effluent of step (d). One reactor tube (21) may suitably be provided with between 1-10 passageways (23). A third tube sheet (32) is present at the lower end of the reactor vessel (44) defining a space (33) which fluidly connects the vessel inlet (38) for the mixture as obtained in step (d) with the inlet of the passageways (23) which penetrate the tube sheet (32) via openings (34) which are preferably larger than the passageway (23) itself. The fact that the passageways are not fixed in the tube sheet (32) is advantageous because it allows the combined reactor tubes (21) and passageways (23) to freely thermally expand in the reactor vessel (44) at start-up and cool down situations. The lower ends of the passageway which extends into the lower space (33) may preferably be made from heat resistant materials like for example ceramics because of the high temperatures present in said space due to the fact that here the mixture as obtained in step (d) enters the CSR reactor via vessel inlet (38).

The outlet opening (35) of the reactor tubes (21) comprising the catalyst bed (22) are positioned just above said tube sheet (32). The steam reforming product being discharged from said opening (35) will enter space (36) defined as the space between tube sheets (40)

and (32). This space (36) fluidly connects the vessel outlet (39) for the steam reforming product with the openings (35). The space (36) may suitably be provided with flow directing baffles which will direct the flow of steam reforming product in a zig zag flow through said space thereby optimising the contact of the hot steam reformer product gas and the external surface of the reactor tubes (21) present in said space. In use part of the steam reforming product being discharged from openings (35) will leave the reactor vessel via outlet (39) and part will leave space (36) via openings (34) to space (33) by operating the reactor such that the pressure in space (36) is higher than the pressure in space (33). In use preferably from 0 to 60 wt% and more preferably from 0 to 40 wt% of the steam reformer product, as being discharged from openings (35), may enter space (33) to be mixed with the effluent of step (d).

Figure 1 further shows a vessel inlet (43) for natural gas and steam, a vessel inlet for a hot gaseous medium (38), a vessel outlet (39) for steam reforming product and a vessel outlet (42) for the gasses, which are emitted from the passageways (23). Tube sheets (40) and (41) are present in order to fix the reactor tubes (21) and to define collecting space (45) for the gasses emitted by the passageways (23) and an inlet space (46) fluidly connecting the vessel inlet (43) for steam and natural gas and the reactor tubes (21) comprising the catalyst bed (22).

Figure 1 also shows a POX reactor vessel (51) provided with a burner (52) to which natural gas and oxygen (50) are provided too. Steam reformer product as discharged at (39) is fed to the POX reactor vessel (51)

via conduit (55) and openings (57) such to perform mixing step (c) at a distance below burner (52) substantially outside the circulating flow around the burner (52), which flow is present in the upper region of the reactor vessel. This results in that no significant conversion of the methane as present in the steam reformer product takes place. Figure 1 also shows a post reforming catalyst bed (53) and a connecting conduit (56) to provide the mixture as obtained in step (d) to step (e). In step (e) this mixture is provided to passageways (23) to supply heat to the steam reforming catalyst bed (22).

The synthesis gas as such obtained by the above process may advantageously be used as feedstock for a Fischer-Tropsch synthesis process, methanol synthesis process, a di-methyl ether synthesis process, an acetic acid synthesis process, ammonia synthesis process or to other processes which use a synthesis gas mixture as feed such as for example processes involving carbonylation and hydroformylation reactions. To steps (a) and (b) preferably recycle gases are fed. These recycle gasses are obtained in, for example the above exemplified, processes which use the synthesis gas as prepared by the process according to the invention. These recycle gasses may comprise C_{1-5} hydrocarbons, preferably C_{1-4} hydrocarbons, more preferably C_{1-3} hydrocarbons. These hydrocarbons, or mixtures thereof, are gaseous at temperatures of 5-30 °C (1 bar), especially at 20 °C (1 bar). Further, oxygenated compounds, e.g. methanol, dimethylether, acetic acid may be present.

The invention is especially directed to the above process for the preparation of hydrogen and carbon monoxide containing gas (synthesis gas), wherein additional steps (f) and (g) are also performed. In

step (f) the synthesis gas is catalytically converted using a Fischer-Tropsch catalyst into a hydrocarbons comprising stream. In step (g) the hydrocarbons comprising stream of step (f) is separated into a hydrocarbon product and a gaseous recycle stream. Suitably the hydrocarbon product are those having 5 or more carbon atoms, preferably having 4 or more carbon atoms and more preferably having 3 or more carbon atoms. The gaseous recycle stream may comprise normally gaseous hydrocarbons produced in the synthesis process, nitrogen, unconverted methane and other feedstock hydrocarbons, unconverted carbon monoxide, carbon dioxide, hydrogen and water.

In step (g) the recycle stream is fed to step (a) and/or (b). Preferably the recycle stream is supplied to the burner of step (a) or directly supplied to the upper region of the partial oxidation reactor.

Optionally part or all of the carbon dioxide present in such a recycle stream is separated from said recycle stream before being fed to step (a). Part of the carbon dioxide may suitably be fed to step (a).

Step (f) and (g) may be performed by the well known Fischer-Tropsch processes which are for example the Sasol process and the Shell Middle Distillate Process. Examples of suitable catalysts are based on iron and cobalt. Typical reactor configurations include slurry reactors and tubular reactors. These and other processes are for example described in more detail in EP-A-776959, EP-A-668342, US-A-4943672, US-A-5059299, WO-A-9934917 and WO-A-9920720.